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Kinetic and Isotherm Studies on Ciprofloxacin an Adsorption using Magnesium Oxide Nanoparticles

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ABSTRACT

The antibiotics along with the sewage, pharmaceutical industries water waste, veterinary clinics and hospital sewages and the agricultural products noticeably enter into the water resources and the environment. The objective of this study was to investigate ciprofloxacin removal efficiency from aqueous solutions by using Magnesium Oxide nanoparticles (MgO). The effects of pH, nanoparticles dose, contact time, initial antibiotic concentration were assessed on ciprofloxacin removal efficiency in laboratory. Under optimal conditions of concentration, the removal efficiency was 85%.and q_m of the MgO nanoparticles was 3.46 mg/g. The process of ciprofloxacin adsorption on MgO nanoparticles was depended on Langmuir adsorption isotherm more than other isotherms. Batch kinetic experiments showed that the adsorption followed Pseudo second -order kinetic model with correlation coefficients greater than 0.978.

INTRODUCTION

Fluoroquinolones are an important class of irresolvable antibiotics used for human beings and animals (Andreozzi *et al*., 2005). The increase of fluoroquinolones concentration in ecosystem results to bacterial resistance and chromosomal mutation (Andreozzi *et al*., 2005; Ji *et al*., 2014). The ciprofloxacin (CIP) is one the antibiotics of fluoroquinolone class used widely in the treatment of urinary, digestive and respiratory systems with good results (Wu *et al*., 2013; Ikehata *et al*., 2006). One of the main reasons for antibiotics purification is bacterial resistance, which is a major threat to human health (Ji *et al*., 2014). So far, the methods applied for CIP elimination are ozonation (Ikehata *et al*., 2006; Ahmadi, 2017a) oxidation (Jiantuan *et al*., 2004), coagulation (Kord Mostafapour *et al*., 2017) and adsorption (Zhang *et al*., 2011).

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One of the main methods is adsorption. The adsorption process is applied widely in industry for eliminating the organic pollutants. The highly used adsorbing materials are the active granulated carbons, but they are very expensive and will be hardly revived (Liao *et al*., 2011; Ahmadi; 2017b). Nanoparticles are a suitable option because of their large surface in order to complete chemical reactions and adsorption of organic compounds (Tajbakhsh *et al*., 2014).

Magnesium oxide nanoparticles (MgO) are a basic oxides group and provided a large range of application in adsorption process (Tajbakhsh *et al*., 2014; Kermani, 2013). The important characteristics of MgO nanoparticles are availability, cheap, non-volatile, non-toxic, stability, adsorption capacity and high reactivity (Kermani *et al*., 2013). It was used as a catalyst in the purification of dangerous, anti-bacterial and resistive materials (Nga *et al*., 2013). The main purpose of this study was the investigation of magnesium oxide nanoparticles efficiency in the removal of CIP from aqueous solution.

The impact of various factors such as the contact time, adsorbent dosage, pH and initial concentration of CIP were studied to determine the optimum condition. The determination of these optimum conditions will cause the enhancement of the efficiency of MgO nanoparticles in CIP removing. Finally, the adsorption isotherm and kinetic models have been studied.

MATERIALS AND METHODS

Materials

The ciprofloxacin (CIP) with molecular weight 331.35 g mol^{-1} from Merck Company (Germany) was purchased. The stock of CIP with a concentration of 1000 mg/L was prepared in distilled water. The chemical structure of CIP is shown in Fig.1. Magnesium oxide (MgO) nanoparticles were purchased from Sigma Co. (US) with a diameter of less than 50 nm, purity of 98% and the effective area of 1236 m^2/g. To determine the exact diameter of the nanoparticle, SEM (HITACHI Model S-3000 H) provided some information about the morphology of adsorbent surface. TEM (FEI Tecnai G2 20 S-TWIN) was used to measure the diameter of nanoparticles.

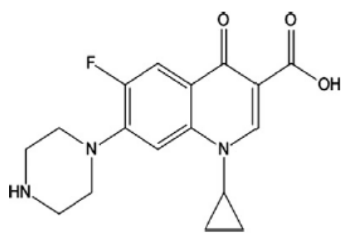

Fig. 1: The chemical structure of CIP.

Batch adsorption experiments

The effect of MgO nanoparticles (0. 1, 0. 3, 0.4, 0.5, 0.8 and 1g/L), contact time (15, 30, 45, 60, 75, 90 and 120 min), pH (2, 3, 6, 9 and 11) and CIP concentrations of 10 to 250 mg/L on CIP removal was investigated. The pH of the water sample was adjusted by adding 0.1 N HCl or 0.1 N NaOH solutions. The initial and final CIP concentrations remaining in solutions were analyzed by a UV–visible recording spectrophotometer was determined at a wavelength of maximum absorbance λ_{max}= 276 nm (Kord Mostafapour *et al*, 2016; Ahmadi-b *et al*., 2017). There are many isotherm models for experimental data analysis and description of equilibrium in adsorption such as Langmuir, Freundlich, and Tempkin (Kord Mostafapour *et al*, 2016). Synthetic equations were used to evaluate the behavior of transferring molecules of adsorbate material in time and the effective variables on reaction rate (Ahmadi-c *et al*., 2017). In this study, the Pseudo first order, Pseudo-second-order and Elovich models were used to evaluate the adsorption process of CIP on the nanoparticle. The equation adsorption kinetics and isotherms are shown in Table1 (Abramović *et al*., 2013).

Removal and sorption capacity of the studied parameters from CIP was calculated based on the following formula (Ahmadi-d *et al*., 2017):

$$\%R = \frac{(C_0 - C_f)}{C_0}100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

Where, C_0 and C_f are the initial and final. C_e is equilibrium concentration (mg/L) of CIP, M weight of adsorbent (g) and V (L) is the volume of the solution.

RESULTS AND DISCUSSION

Figs. 2 and 3 display the SEM and TEM images of MgO nanoparticles respectively. For, the special level was equal to 1236 m^{۲}/g indicating a suitable special level.

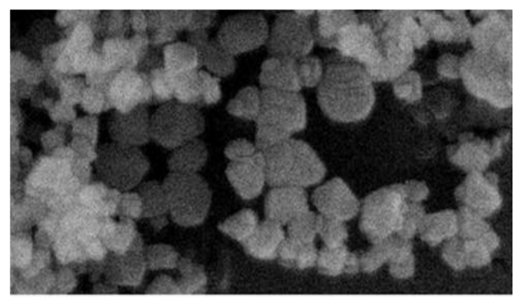

Fig. 2: SEM image on MgO nanoparticles.

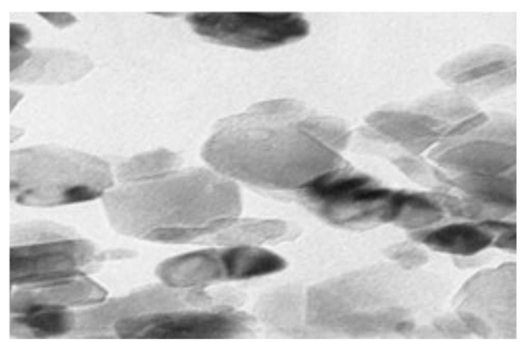

Fig. 3: TEM image on MgO nanoparticles.

Table 1: The equations of isotherms and kinetic.

Model	isotherms		
	Langmuir	**Freundlich**	**Tempkin**
	$\frac{ce}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_l}$	$Logq_e = \frac{1}{n} LogC_e + Logk_f$	$q_e = B_1 Ln(A_T) + B_1 In(C_e)$
Model	**kinetics**		
	Pseudo first order	**Pseudo second order**	**Elovich**
	$Log(q_e - q_t) = Log(q_e) - \frac{k_1}{2.303} t$	$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \frac{t}{q\ e}$	$q_e = \frac{1}{\beta} Ln(\beta\alpha) + \frac{1}{\beta} Int$

Effect of pH on the MgO adsorption

The results showed (Fig. 4) that increase of pH to 6 lead to increase of removing CIP. Moreover, the removal percentage increased from pH 2 to pH 6 (60% to 80%). Increased removal rate at pH 6 was related to pH_{zpc} and pK_a. The level of pK_a for CIP is 5.7 and the level of pH_{zpc} nanoparticles of MgO is 12.4 (Kord Mostafapour *et al*, 2017; Tajbakhsh *et al*., 2014). It was related to pH_{zpc} and pK_a. The point of zero charge is the point where the charge on catalyst surface is zero. In the pH less than pH_{zpc}, the catalyst had positive charge that increase of pH to 6, Electrostatic adsorption between CIP negative ions and positive charged MgO nanoparticles increased, therefore, the efficiency of removal increased (Venkatesha *et al*., 2013; Moussavi *et al*., 2011).

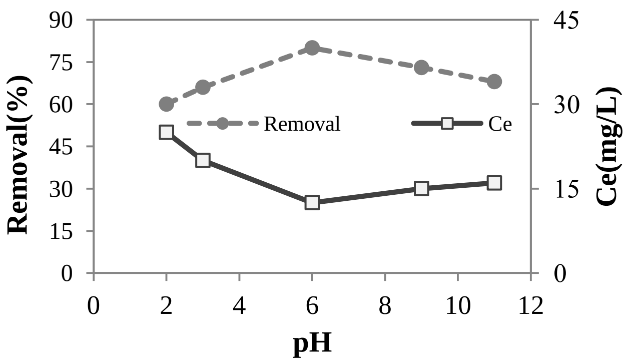

Fig.4: Effect of pH on percentage removal of CIP (Time: 60 min, dosage: 0.1g/L, CIP concentration: 100 mg/L).

Effect of initial ciprofloxacin concentration

To determine the effect of initial CIP concentration on the adsorption process the initial concentration of CIP was varied from 10 to 250 mg/L at the optimum pH, adsorbent dose 0.1g/L and contact time 60 min. As presented in Fig. 5, CIP removal efficiency decreased with increasing of initial CIP concentration. So, maximum efficiency was achieved at initial CIP concentration 10 mg/L (85%). The main reason was an increase of contact and collision between adsorbent and adsorbate (Moussavi *et al*., 2011).

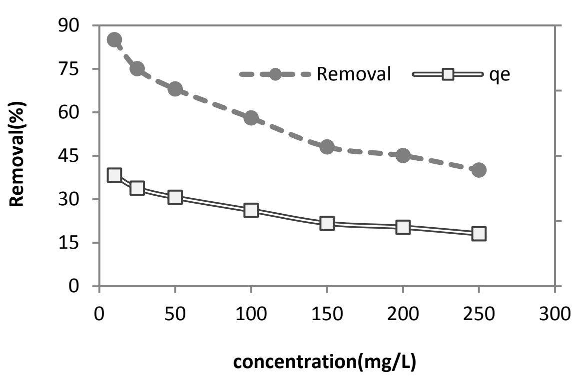

Fig. 5: Effect of initial CIP concentration on percentage removal of CIP (Time: 60 min, pH: 6, dosage: 0.1g/L).

Effects of adsorbent dose on the MgO adsorption

The Fig.6, the adsorbent concentration increased from 0.1 to 1g/L for improved concentration 10 mg/L CIP, the efficiency increased from 60% to 83%; in fact the level of deletion significantly depends on active places and by increasing the dosage of nanoparticle to an appropriate level, the deletion efficiency will also be increased (Tamimi *et al*., 2008).

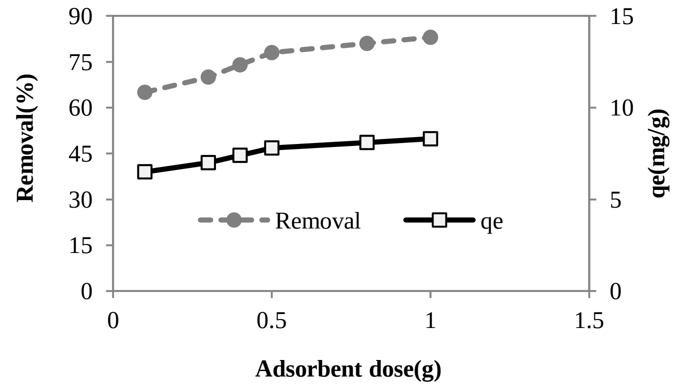

Fig. 6: Effect of adsorbent dose on percentage removal of CIP (Time: 60 min, pH: 6, CIP concentration: 25mg/L).

Effects of contact time on the MgO adsorption

The efficiency of antibiotic deletion at the contact time 60 min and the concentration of antibiotic (10mg/L) have increased 85 % (Fig. 7). By increasing the contact time, the efficiency of antibiotic deletion will be increased. The reason for increasing the deletion efficiency at the early hours is that by passing the time the made cavity and corrosion on nanoparticle level will be expanded and so increase the cross section of adsorption and efficiency (Samadi *et al*., 2013). The reason for decreasing removal efficiency by enhancement of antibiotic concentration is saturation of active places of adsorption (Samadi *et al*., 2013; Zhang, 2017).

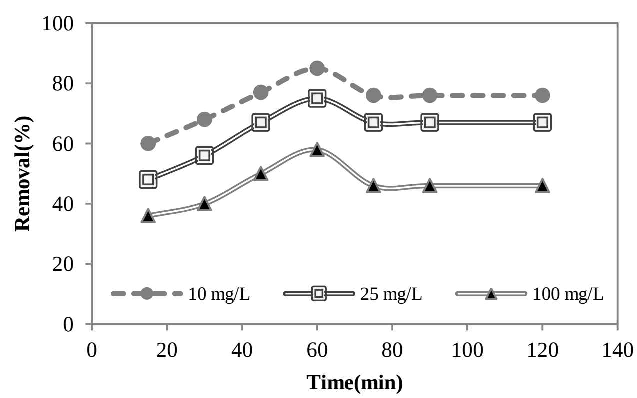

Fig. 7: Effect of time on percentage removal of CIP (pH: 6, dosage: 1g/L, CIP concentration: 25mg/L).

The isothermal models and adsorption kinetics are shown in Table 2 and 3.The results showed that ciprofloxacin fitted according to Langmuir isotherm model (R^2=0.96). The R^2 of kinetic models suggested that the pseudo-second -order model mechanism is predominant which means the uptake process follows the pseudo second-order expression with correlation coefficients were always greater of 0.9785.

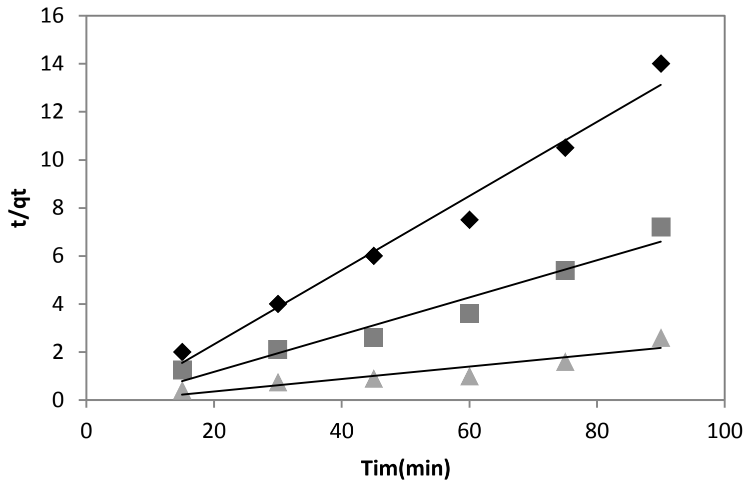

Fig.8: Kinetic isotherms pseudo-second-order

Table 2: The adsorption isotherms constants for the absorption CIP.

C_0(mg/L)	Langmuir				Freundlich			Tempkin		
	q_m	k_L	R^2	R_L	n	k_f	R^2	B_T	A_T	R^2
10	3.46	0.08	0.9613	0.55	1.8	39.8	0.93	0.24	0.129	0.934

Table 3: The adsorption kinetic model constants for the absorption CIP.

C_0(mg/L)	Pseudo-first order			Pseudo-second order			Elovich		
	K_1	qe	R^2	K_2	qe	R^2	α	β	R^2
10	0.04	0.2	0.862	0.02	6.5	0.978	6.9	0.93	0.785
25	0.006	4.48	0.539	0.006	12.91	0.947	14.4	0.41	0.768
100	0.004	29.71	0.362	0.0006	38.6	0.859	146.6	0.19	0.28

CONCLUSION

In this study, the adsorption of CIP onto MgO nanoparticles has been investigated. The results of this study indicate that optimum conditions for the operation of the MgO nanoparticles with CIP concentration of 10 mg/L, pH of 6, MgO dose 1 g/L and contact time of 60 min can remove a large impact on the concentration of CIP in water. According to the results, under optimal conditions of concentration, the removal efficiency was 85%.and q_m of the MgO nanoparticles was 3.46 mg/g. The process of CIP adsorption on MgO nanoparticles was depended on Langmuir absorption isotherm more than other isotherms. Batch kinetic experiments showed that the adsorption followed pseudo-second-order kinetic model with correlation coefficients greater than 0.978.

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Conflict of Interests: There are no conflicts of interest.

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